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SYNTHESIS OF NEW BENZOXAZINE MONOMERS AND POLYMERS

Relevance of the research.

The development of modern technology and its industries such as aerospace, electronics, engineering and others requires the creation of new polymer composite materials (PCM) with improved mechanical properties, durability, thermal characteristics and incombustibility. At the same time, the economic component of PCM production is important: the availability of initial monomers and oligomers, and their cost. Another important factor is the manufacturability of PCM production.

The main binders for PCM were phenol- and amino-formaldehyde oligomers in the 40s-60s, but epoxy resins began to be widely used after the 1960s. Recently researchers pay special attention to Polybenzoxazines – "relatives" of phenolic and amino-formaldehyde resins. They are obtained from the similar raw materials – (amines, phenols, formaldehyde) by the one-pot reaction of these substances.

A distinctive feature of mono- and oligobenzoxazines is their ability for thermal polymerization at temperatures above 200 °C without the release of volatile by-products that prevent the formation of a dense homogeneous structure in PCM.

Despite the abundance of scientific works on the synthesis and use of benzoxazine monomers, oligomers, and polymers, the mechanism of polymerization of the benzoxazine ring and ways to control the properties of the resulting polymers is still not established.

The general goal of this work is to clarify the mechanism of polymerization of mono- and dibenzoxazines, to establish the structure of the resulting polymers, to reveal their properties and possibilities of controlling them by selecting the starting compounds and varying the polymerization conditions.

Tasks:

1. To reveal the features of the polymerization of the model monobenzoxazine, the composition and structure of the resulting polymer.

2. Evaluate the role of side transformations in the thermal polymerization of monobenzoxazine.

3. Synthesize dibenzoxazines based on diamines, establish their structure and optimal polymerization conditions.

4. To evaluate the rheological, thermal and other characteristics of polybenzoxazines and possible ways of their processing into PCM.

Scientific novelty.

On the example of the model compound 3-phenyl-2,4-dihydro-1,3-benzoxazine, using the methods of IR, ^{1}H and ^{13}C NMR spectroscopy, as well as X-ray photoelectron spectroscopy, the structure of the resulting polybenzoxazine was established. Despite to the known data, the polymerization of cyclic compounds turned out to be three-dimensional, insoluble, infusible product.

It was discovered that side reactions of the active center with the formation of methylol groups and their participation in structure formation are responsible for the formation of a three-dimensional polymer.

The optimal synthesis conditions and the structure of dibenzoxazines based on 4,4'-diaminodiphenylmethane and its chlorine derivative (3,3'-dichloro-4,4'-diaminodiphenylmethane) were established by using IR, ^{1}H and ^{13}C NMR spectroscopy.

Based on the analysis of the thermal and rheological characteristics of dibenzoxazines, it was revealed that they have a wide temperature interval between the onset of flow and the formation of a three-dimensional polymer. Which makes it possible to process dibenzoxazines by modern methods.

Theoretical and practical significance of the work.

Establishing the features of the compounds with benzoxazine rings polymerization expands the existing ideas about the polymerization of heterocycles and the side reactions that occur in this case.

Due to the availability, relatively low cost of the starting components, and the possibility of synthesizing mono- and dibenzoxazines using standard equipment, they are of interest for use in PCMs for various purposes. The promise of

polybenzoxazines is confirmed by the possibility of their processing into products using modern methods.

The main provisions for the defense:

– Synthesis of model monobenzoxazine 3-phenyl-2,4-dihydro-1,3-benzoxazine and study of its polymerization products by X-ray photoelectron spectroscopy.

– Synthesis of dibenzoxazines based on aromatic diamines of various structures, study of their structure, thermal and rheological properties.

– Selection of optimal conditions for the preparation of benzoxazines based on diamines.

– Establishment of regularities in the formation of polymers during thermal polymerization of benzoxazine monomers and oligomers with opening of the oxazine ring.